

## Appendix EE

### Emissions Estimation Procedures for Process Vents

The following paragraphs briefly summarize the techniques for calculating uncontrolled and controlled emissions by emission estimation procedures for the following emission episodes:

- . Vapor Displacement
- . Purging
- . Heating
- . Depressurization
- . Vacuum Systems
- . Gas Evolution
- . Air Drying
- . Empty Vessel Purging

Uncontrolled emissions calculations for the above source types are given in sections 63.1257(d)(2)(i) (A) through (H), respectively, and controlled emissions techniques in 63.1257(d)(3)(i)(B) (1) through (8), respectively. If the owner or operator determines that these equations are not appropriate for his/her operations, the regulations at 63.1257(d)(2)(ii) allow for the use of other engineering assessments to determine uncontrolled HAP emissions. If alternative equations or engineering assessments will be conducted, the owner or operator must document all data, assumptions, and procedures in the Precompliance Report.

The following discussion refers to equation numbers found in 63.1257(d) (Numbers 11 - 43). Except where variations are noted, individual HAP partial pressures in multicomponent systems shall be determined by the following methods: If the components are miscible in one another, use Raoult's law to calculate the partial pressures; if the solution is a dilute aqueous mixture, use Henry's law to calculate partial pressures; if Raoult's law or Henry's law are not appropriate or available, use experimentally obtained activity coefficients or models such as the group-contribution models, to predict activity coefficients, or assume the components of the system behave independently and use the summation of all vapor pressures from the HAP as the total HAP partial pressure. Chemical property data can be obtained from standard reference texts.

**Vapor Displacement-Uncontrolled Emissions:** Calculating HAP emissions from vapor displacement due to material transfer is accomplished according to Equation 11. The following values are needed:

- . Volume of Gas displaced by vessel (V),
- . Temperature of vessel vapor space (T),
- . Partial Pressure of each HAPs (may be calculated using Raoult's Law) ( $P_i$ ),
- . Molecular Weight of each HAP ( $MW_i$ ),

- . Universal gas constant (R), and
- . Total number of HAPs (n).

**Vapor Displacement-Controlled Emissions:** Same as above (using equation 11) except  $T$  = temperature of the receiver and the HAP partial pressures are determined at the temperature of the receiver.

**Purging-Uncontrolled Emissions:** Calculating HAP emissions from purging is accomplished according to Equation 12. The following values are needed:

- . Purge flow rate at the temperature and pressure of the vessel vapor space (V),
- . Temperature of the vessel vapor space; absolute (T).
- . Partial pressure of the individual HAP ( $P_i$ ), which may be calculated using Raoult's Law
- . Partial pressure of individual condensable VOC compounds (including HAP) ( $P_j$ ), which may be calculated using Raoult's Law
- . Pressure of the vessel vapor space ( $P_T$ ), which may be set to 760 mmHg for atmospheric conditions
- . Molecular weight of the individual HAP ( $MW_i$ ),
- . Time of purge (t),
- . Number of HAP compounds in the emission stream (n),
- . Number of condensable VOC compounds (including HAP) in the emission stream (m), and
- . Ideal gas law constant (R).

HAP vapor concentration must be assumed to be 25% of the saturated value when the purge rate is greater than 100 standard cubic feet per minute (scfm).

**Purging - Controlled Emissions:** Same as above (using equation 12) except  $T$  = temperature of the receiver and HAP partial pressures determined at the temperature of the receiver.

**Heating - Uncontrolled Emissions:** There are three methods given in Section 63.1257(d)(2)(i)C for calculating HAP emissions from heating a vessel. For heating processes where the vessel contents are heated to  $\leq 10^\circ\text{K}$  below the content's boiling point (Scenario 1), equation 13 or 14 or 18 must be used. For heating processes where the vessel contents are heated to within  $10^\circ\text{K}$  of the content's boiling point (but below the boiling point) (Scenario 2), equation 13 or 14 or 18 must be used. However, in equations 13 and 14,  $T_2$  must be  $10^\circ\text{K}$  below the boiling point. For Scenario 2, the O/O can use Equation 14 to calculate two increments. If the contents are heated to boiling, the vessel must be operated with a properly operated process condenser. A demonstration that the process condenser is properly operated is required if: (1) the process condenser is not followed by an air pollution control device, or (2) the air pollution control device following the process condenser is not a condenser or is not meeting the

alternative standard of §63.1254(c). HAP emissions are assumed to be zero if a process condenser is properly operated and documented as follows:

- . show that the exhaust gas temperature is less than the boiling point of the substance(s) in the vessel, or
- . perform a material balance around the condenser and show that at least 99% of the material vaporized while boiling is condensed.

Several calculation options are given for each of the 2 heating scenarios described above. The owner/operator should review the equations and decide which is best for his given situation. These procedures are summarized below:

#### Equation

<u>No.</u>	<u>Description</u>
13 or 14 or 18	<i>Scenario 1 = Final Temp is <math>\leq 10^{\circ}\text{K}</math> below HAP boiling point</i> - These equations are similar and the choice of which to use is left up to the owner/operator. Both of them calculate HAP emissions based on <u>initial &amp; final pressure</u> of the vessel, <u>initial &amp; final temperatures</u> , average HAP MW calculated by weighting each <u>HAP's MW</u> by the respective <u>HAP partial pressure</u> (Eq. 14 only), <u>HAP vapor pressure &amp; mole fraction</u> in the liquid phase, and <u>condensable VOC vapor pressure &amp; mole fraction</u> in the liquid phase. Equation 18 calculates HAP emissions based on initial and final HAP partial pressures, total pressure of the vessel, initial and final temperatures, average HAP MW and the volume of free space in the vessel.
15 - 17	Supporting equations for 13 & 14. NOTE: Eq. 17 supports Eq. 14 only.
19-20	Supporting equations for 18.
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	<i>Scenario 2 = Final Temp is <math>&gt; 10^{\circ}\text{K}</math> below HAP boiling point</i> - The Owner/Operator has a choice of 4 calculation methods for this scenario as follows:
13, or	1. Use equation 13 with <u>parameters</u> (vapor pressures, $T_2$ , $Pa_2$ ) determined <u>at <math>10^{\circ}\text{K}</math> below the boiling point</u> .
14, or	2. Use equation 14 with <u>parameters</u> (HAP partial pressures, $T_2$ , $Pa_2$ ) determined <u>at <math>10^{\circ}\text{K}</math> below the boiling point</u>
14	3. Use Equation 14 to calculate emissions as the sum of emissions for 2 discrete temperature increments (i.e, <u>(initial temp to <math>10^{\circ}\text{K}</math> below BP)</u> + <u>(<math>10^{\circ}\text{K}</math> below BP to the lower of the final temperature or <math>5^{\circ}\text{K}</math> below the</u>

BP)

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4. Same as above.

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**Heating - Controlled Emissions:** Use equation 13 or 37. In equation 13 HAP vapor pressures shall be determined at the temperature of the receiver. In equation 13 and 37, the average HAP molecular weight shall be calculated using the HAP partial pressures at the temperature of the receiver.

**Depressurization - Uncontrolled Emissions:** There is a choice of three techniques for calculating HAP emissions from depressurization events. The owner/operator should review the equations and decide which is best for his given situation. These procedures are summarized below:

- |              |   |
|--------------|---|
| 21-26, 17    | 1. The first technique calculates HAPs emissions using the ideal gas law as a function of the volume of non-condensable gas produced, ratio of moles of non-condensable gas to moles of HAPs, HAP MW, pressure, temperature and universal gas constant. Equation input parameters include <u>free volume</u> of the vessel, <u>condensable VOC</u> (including HAPs) <u>vapor pressure &amp; mole fraction</u> , <u>HAP vapor pressure &amp; mole fraction</u> , and <u>initial &amp; final pressure</u> of the vessel. The HAP partial pressure may be calculated using Raoult's Law. |
| 27-31, 23-24 | 2. HAPs emissions are calculated by this method by multiplying the average HAP-to-non-condensable gas mole ratio by the number of moles of non condensable gas released during the event. Equation inputs are <u>initial &amp; final pressure</u> , <u>temperature</u> , <u>condensable VOC vapor pressure &amp; mole fraction</u> , <u>mole fraction of HAPs</u> , and <u>average HAP molecular weight</u> .   |
| 32           | 3. Equation 32 presents another approach to calculating HAPs emissions from depressurization. Parameter inputs include <u>vessel volume</u> , <u>temperature</u> , <u>initial &amp; final pressure</u> , <u>partial pressure of individual HAP compounds</u> , <u>molecular weight of individual HAP compounds</u> .  |

**Depressurization - Controlled Emissions:** Use equation 38 with the initial and final volumes of noncondensable gas in the vessel, adjusted to the pressure of the receiver, calculated using equations 39 and 40. Initial and final partial pressures of noncondensable gas in the vessel are calculated using equations 41 and 42.

**Vacuum Systems - Uncontrolled Emissions:** HAPS emissions from vacuum systems may be calculated using equation 33 if the air leakage rate is known or can be calculated. Values needed are

- . Absolute pressure of receiving vessel or ejector outlet conditions ( $P_{\text{system}}$ ),
- . Partial pressure of HAP at receiver temperature ( $P_i$ ), or the ejector outlet conditions
- . Partial pressure of condensable at receiver temperature ( $P_j$ ) or the ejector outlet conditions
- . Total air leak rate in the system ( $La$ ),
- . Molecular weight of non-condensable gas ( $MW_{nc}$ ),
- . Molecular weight of the individual HAP with partial pressures calculated at receiver or ejector outlet temperature, as appropriate ( $MW_i$ ),
- . Time of the vacuum operation.

**Vacuum Systems - Controlled Emissions:** Use equation 33 to calculate controlled emissions from vacuum systems.

**Gas Evolution - Uncontrolled Emissions:** Use equation 12 with Volumetric Flow ( $V$ ) determined by equation 34. Parameter inputs are:

- . Mass flow rate of gas evolution ( $W_g$ ),
- . Temperature at the exit, absolute ( $T$ ),
- . Vessel pressure ( $P_T$ ),
- . Molecular weight of the evolved gas ( $MW_g$ )
- . Ideal gas law constant ( $R$ ),

**Gas Evolution - Controlled Emissions:** Use equation 12 with  $V$  calculated using equation 34 and  $T$  set to equal the temperature of the receiver and the HAP partial pressures determined at the receiver temperature. The term for time,  $t$  in equation 12, is not need for the purposes of this calculation.

**Air Drying - Uncontrolled Emissions:** Use equation 35 to calculate HAPs emissions per batch of air dried solids with parameter inputs as follows:

- . Mass of dry solids ( $B$ ),
- . HAP in material entering dryer, weight percent ( $PS_1$ ), and
- . HAP in material exiting dryer, weight percent ( $PS_2$ )

**Air Drying - Controlled Emissions:** Same as above (use equation 11) with  $V$  equal to the air flow rate and  $P_i$  determined at the temperature of the receiver.

**Empty Vessel Purging - Uncontrolled Emissions:** Use equation 36 with the following inputs:

- Volume of empty vessel ( $V$ ),
- Temperature of the vessel vapor space ( $T$ ),
- Partial pressure of the individual HAP at the beginning of the purge ( $P_i$ ),
- Flowrate of the purge gas ( $F$ ), and
- Duration of the purge ( $t$ )

Note that the term  $e^{-Ft/v}$  can be assumed to be zero.

**Empty Vessel Purging - Controlled Emissions:** Use equation 43 with the following inputs:

- Volume of empty vessel (V),
- Temperature of the vessel vapor space at beginning of purge ( $T_1$ )
- Temperature of the receiver ( $T_2$ ),
- Partial pressure of the individual HAP at the beginning of the purge ( $P_i$ ) $_{T1}$ ,
- Partial pressure of the individual HAP at the receiver temperature ( $P_i$ ) $_{T2}$ ,
- Flowrate of the purge gas (F), and
- Duration of the purge (t)

**Emissions Estimation Equations for Uncontrolled Sources (11-36) and Controlled Sources (37-43)**

No.	Equation
11	<p>Vapor Displacement</p> $E = \frac{(V)}{(R)(T)} \times \sum_{i=1}^n (P_i)(MW_i)$ <p> E = mass of HAP emitted  V = volume of gas displaced from the vessel  R = ideal gas law constant  T = temperature of the vessel vapor space; absolute  <math>P_i</math> = partial pressure of the individual HAP  <math>MW_i</math> = molecular weight of the individual HAP  n = number of HAP compounds in the emission stream  i = identifier for a HAP compound </p>

**Emissions Estimations Equations for Uncontrolled Sources (11-36) and Controlled Sources (37-43) (continued)**

No.	Equation
12	$E = \sum_{i=1}^n P_i MW_i \times \frac{(V)(t)}{(R)(T)} \times \frac{P_T}{P_T - \sum_{j=1}^m (P_j)}$ <p>Purging:</p> <p> E = mass of HAP emitted  V = purge flow rate at the temperature and pressure of the vessel vapor space  R = ideal gas law constant  T = temperature of the vessel vapor space; absolute  <math>P_i</math> = partial pressure of the individual HAP </p>

	<p> <math>P_j</math> = partial pressure of individual condensable VOC compounds (including HAP)  <math>P_T</math> = pressure of the vessel vapor space  <math>MW_i</math> = molecular weight of the individual HAP  <math>t</math> = time of purge  <math>i</math> = identifier for a HAP compound  <math>j</math> = identifier for a condensable compound  <math>n</math> = number of HAP compounds in the emission stream  <math>m</math> = number of condensable VOC compounds (including HAP) in the emission stream </p>
13	<p>Heating (1)</p> $E = \frac{\sum_{i=1}^n ((P_i^*)(x_i)(MW_i))}{760 - \sum_{j=1}^m ((P_j^*)(x_j))} \times \Delta n$ <p> <math>E</math> = mass of HAP vapor displaced from the vessel being heated  <math>x_i</math> = mole fraction of each HAP in the liquid phase  <math>x_j</math> = mole fraction of each condensable VOC (including HAP) in the liquid phase  <math>(P_i^*)</math> = vapor pressure of each HAP in the vessel headspace, mmHg  <math>(P_j^*)</math> = vapor pressure of each condensable VOC (including HAP) in the vessel headspace, mmHg  <math>760</math> = atmospheric pressure, mmHg  <math>MW_i</math> = molecular weight of the individual HAP  <math>n</math> = number of HAP compounds in the displaced vapor  <math>m</math> = number of condensable VOC compounds (including HAP) in the displaced vapor  <math>\Delta n</math> = number of moles of non-condensable gas displaced, as calculated using Equation 15 of this subpart  <math>i</math> = identifier for a HAP compound </p>
14	$E = \frac{\frac{\sum_{i=1}^n (P_i)_{T1}}{Pa_1} + \frac{\sum_{i=1}^n (P_i)_{T2}}{Pa_2}}{2} \times \Delta n \times MW_{HAP}$ <p> <math>Pa_n</math> = partial pressure of non-condensable gas in the vessel headspace at the initial (n=1) and final (n=2) temp.  <math>(P_i)_{Tn}</math> = partial pressure of each HAP in the vessel headspace at initial (<math>T_1</math>) and final (<math>T_2</math>) temperature. [For use in Equation 13, replace <math>(P_i)_{T1} + (P_i)_{T2}</math> with <math>P_i</math> at the temperature used to calculate vapor pressure of HAP in Equation 13.]  Heating (2)  (same as Equation 13) </p>

15	$\Delta h = \frac{V}{R} \left[ \left( \frac{Pa_1}{T_1} \right) - \left( \frac{Pa_2}{T_2} \right) \right]$ <p>Heating (3)</p> <p><math>\theta\eta</math> = number of moles of gas displaced</p> <p><math>V</math> = volume of free space in the vessel</p> <p><math>R</math> = ideal gas law constant</p> <p><math>Pa_1</math> = initial noncondensable gas pressure in the vessel, as calculated using Equation 16</p> <p><math>Pa_2</math> = final noncondensable gas pressure in the vessel, as calculated using Equation 16</p> <p><math>T_1</math> = initial temperature of vessel, absolute</p> <p><math>T_2</math> = final temperature of vessel, absolute</p>
16	$Pa_n = P_{atm} - \sum_{j=1}^m (P_j)_{Tn}$ <p>Heating (4):</p> <p><math>Pa_n</math> = partial pressure of noncondensable gas in the vessel headspace at initial (n=1) and final (n=2) temperature</p> <p><math>P_{atm}</math> = atmospheric pressure (when <math>\theta?</math> is used in Equation 13 of this subpart, <math>P_{atm}</math> may be set equal to 760 mmHg for any vessel)</p> <p><math>(P_j)_{Tn}</math> = partial pressure of each condensable volatile organic compound (including HAP) in the vessel headspace at the initial temperature (n=1) and final (n=2) temperature</p> <p><math>m</math> = number of condensable VOC compounds (including HAP) in the displaced vapor</p> <p><math>j</math> = identifier for a condensable compound</p>
17	$MW_{HAP} = \frac{\sum_{i=1}^n ((P_i)_{T_1} + (P_i)_{T_2}) MW_i}{\sum_{i=1}^n ((P_i)_{T_1} + (P_i)_{T_2})}$ <p>Heating (5):</p> <p><math>MW_{HAP}</math> = average molecular weight of HAP in the displaced gas</p> <p><math>(P_i *)</math> = vapor pressure of each HAP in the vessel headspace at any temperature between the initial and final heatup temperatures, mmHg</p> <p><math>(P_i)_{Tn}</math> = partial pressure of each HAP in the vessel headspace at initial (<math>T_1</math>) and final (<math>T_2</math>) temperature [For use in Equation 13, replace <math>(P_i)_{T_1} + (P_i)_{T_2}</math> with <math>P_i</math> at the temperature used to calculate vapor pressure of HAP in Equation 13]</p> <p><math>MW_i</math> = molecular weight of each HAP</p> <p><math>n</math> = number of HAP compounds in the emission stream</p>
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	$E = MW_{HAP} \times \left( N_{avg} \times \ln \left( \frac{P_T - \sum_{i=1}^n (P_{i,1})}{P_T - \sum_{i=1}^n (P_{i,2})} \right) - (n_{i,2} - n_{i,1}) \right)$ <p>Heating (6):</p> <p>E = mass of HAP vapor displaced from the vessel being heated</p> <p>N<sub>avg</sub> = average gas space molar volume during the heating process</p> <p>P<sub>T</sub> = total pressure in the vessel</p> <p>P<sub>i,1</sub> = partial pressure of the individual HAP compounds at T<sub>1</sub></p> <p>P<sub>i,2</sub> = partial pressure of the individual HAP compounds at T<sub>2</sub></p> <p>MW<sub>HAP</sub> = average molecular weight of the HAP compounds</p> <p>n<sub>i,1</sub> = number of moles of condensable in the vessel headspace at T<sub>1</sub></p> <p>n<sub>i,2</sub> = number of moles of condensable in the vessel headspace at T<sub>2</sub></p> <p>n = number of HAP compounds in the emission stream</p>
19	$N_{avg} = \frac{VP_T}{2R} \left( \frac{1}{T_1} + \frac{1}{T_2} \right)$ <p>Heating (7):</p> <p>N<sub>avg</sub> = average gas space molar volume during the heating process</p> <p>V = volume of free space in vessel</p> <p>P<sub>T</sub> = total pressure in the vessel</p> <p>R = ideal gas law constant</p> <p>T<sub>1</sub> = initial temperature of the vessel</p> <p>T<sub>2</sub> = final temperature of the vessel</p>
20	$(n_{i,2} - n_{i,1}) = \frac{V}{(R)(T_2)} \sum_{i=1}^n P_{i,2} - \frac{V}{(R)(T_1)} \sum_{i=1}^n P_{i,1}$ <p>Heating (8):</p> <p>V = volume of free space in vessel</p> <p>R = ideal gas law constant</p> <p>T<sub>1</sub> = initial temperature in the vessel</p> <p>T<sub>2</sub> = final temperature in the vessel</p> <p>P<sub>i,1</sub> = partial pressure of the individual HAP compounds at T<sub>1</sub></p> <p>P<sub>i,2</sub> = partial pressure of the individual HAP compounds at T<sub>2</sub></p> <p>n = number of HAP compounds in the emission stream</p>
21	<p>Depressurization (1):</p> $V_{nc1} = \frac{VP_{nc1}}{760}$ <p>V<sub>nc1</sub> = initial volume of noncondensable gas in the vessel</p>

	<p> <math>V_{nc2}</math> = final volume of noncondensable gas in the vessel  <math>V</math> = free volume in the vessel being depressurized  <math>P_{nc1}</math> = initial partial pressure of the noncondensable gas, as calculated using Equation 23 of this subpart, mmHg  <math>P_{nc2}</math> = final partial pressure of the noncondensable gas, as calculated using Equation 24 of this subpart, mmHg  760 = atmospheric pressure, mmHg </p>
22	$V_{nc2} = \frac{VP_{nc2}}{760}$ <p>Depressurization (2): (same as equation 21)</p>
23	$P_{nc1} = P_1 - \sum_{j=1}^m (P_j^*)(x_j)$ <p>Depressurization (3):  <math>P_{nc1}</math> = initial partial pressure of the noncondensable gas  <math>P_{nc2}</math> = final partial pressure of the noncondensable gas  <math>P_1</math> = initial vessel pressure  <math>P_2</math> = final vessel pressure  <math>P_j^*</math> = vapor pressure of each condensable VOC (including HAP) in the emission stream  <math>x_j</math> = mole fraction of each condensable VOC (including HAP) in the emission stream  <math>m</math> = number of condensable VOC compounds (including HAP) in the emission stream</p>
24	$P_{nc2} = P_2 - \sum_{j=1}^m (P_j^*)(x_j)$ <p>Depressurization (4): (same as equation 23)</p>
25	$n_{Ri} = \frac{\left( \frac{P_{nc1}}{\sum_{i=1}^n (P_i^*)(x_i)} + \frac{P_{nc2}}{\sum_{i=1}^n (P_i^*)(x_i)} \right)}{2}$ <p>Depressurization (5):  <math>n_{Ri}</math> = average ratio of moles of noncondensable to moles of individual HAP  <math>P_{nc1}</math> = initial partial pressure of the noncondensable gas, as calculated using Equation 20 of this subpart  <math>P_{nc2}</math> = final partial pressure of the noncondensable gas, as calculated using Equation 21</p>

	<p>of this subpart</p> <p><math>P_i^*</math> = vapor pressure of each individual HAP</p> <p><math>x_i</math> = mole fraction of each individual HAP in the liquid phase</p>
26	$E = (V_{nc1} - V_{nc2}) \times \frac{P_{atm}}{RT} \times \sum_{i=1}^n \frac{MW_i}{n_{Ri}}$ <p>Depressurization (6):</p> <p><math>E</math> = mass of HAP emitted</p> <p><math>V_{nc1}</math> = initial volume of noncondensable gas in the vessel, as calculated using Equation 21 of this subpart</p> <p><math>V_{nc2}</math> = final volume of noncondensable gas in the vessel, as calculated using Equation 22 of this subpart</p> <p><math>n_{Ri}</math> = average ratio of moles of noncondensable to moles of individual HAP, as calculated using Equation 25 of this subpart</p> <p><math>P_{atm}</math> = atmospheric pressure, standard</p> <p><math>R</math> = ideal gas law constant</p> <p><math>T</math> = temperature of the vessel, absolute</p> <p><math>MW_i</math> = molecular weight of each HAP</p>
27	$n_{HAP} = \frac{(Y_{HAP})(V)(P_1)}{R T}$ <p>Depressurization (7):</p> <p><math>Y_{HAP}</math> = mole fraction of HAP (the sum of the individual HAP fractions, <math>SY_i</math>)</p> <p><math>V</math> = free volume in the vessel being depressurized</p> <p><math>P_1</math> = initial vessel pressure</p> <p><math>R</math> = ideal gas law constant</p> <p><math>T</math> = vessel temperature, absolute</p>
28	$n_1 = \frac{VP_{nc1}}{RT}$ <p>Depressurization (8):</p> <p><math>n_1</math> = initial number of moles of noncondensable gas in the vessel</p> <p><math>n_2</math> = final number of moles of noncondensable gas in the vessel</p> <p><math>V</math> = free volume in the vessel being depressurized</p> <p><math>P_{nc1}</math> = initial partial pressure of the noncondensable gas, as calculated using Equation 23 of this subpart</p> <p><math>P_{nc2}</math> = final partial pressure of the noncondensable gas, as calculated using Equation 24 of this subpart</p> <p><math>R</math> = ideal gas law constant</p> <p><math>T</math> = temperature, absolute</p>
29	Depressurization (9):

	$n_2 = \frac{VP_{nc2}}{RT}$ <p>same as equation 28)</p>
30	<p>Depressurization (10):</p> $n_{HAP} = \frac{\left( \frac{n_{HAP,1}}{n_1} + \frac{n_{HAP,2}}{n_2} \right)}{2} [n_1 - n_2]$ <p> <math>n_{HAP}</math> = moles of HAP emitted  <math>n_1</math> = initial number of moles of noncondensable gas in the vessel, as calculated using Equation 28 of this subpart  <math>n_2</math> = final number of moles of noncondensable gas in the vessel, as calculated using Equation 29 of this subpart </p>
31	$E = n_{HAP} * MW_{HAP}$ <p> Depressurization (11):  <math>E</math> = mass of HAP emitted  <math>n_{HAP}</math> = moles of HAP emitted, as calculated using Equation 30 of this subpart  <math>MW_{HAP}</math> = average molecular weight of the HAP as calculated using Equation 17 of this subpart </p>
32	$E = \frac{V}{(R)(T)} \times \ln \left( \frac{P_1 - \sum_{j=1}^m (P_j)}{P_2 - \sum_{j=1}^m (P_j)} \right) \times \sum_{i=1}^n (P_i)(MW_i)$ <p> Depressurization (12):  <math>V</math> = free volume in vessel being depressurized  <math>R</math> = ideal gas law constant  <math>T</math> = temperature of the vessel, absolute  <math>P_1</math> = initial pressure in the vessel  <math>P_2</math> = final pressure in the vessel  <math>P_j</math> = partial pressure of the individual condensable compounds, including HAP  <math>MW_i</math> = molecular weight of the individual HAP compounds  <math>n</math> = number of HAP compounds in the emission stream  <math>m</math> = number of condensable compounds (including HAP) in the emission stream  <math>i</math> = identifier for a HAP compound  <math>j</math> = identifier for a condensable compound </p>
33	Vacuum Systems:

	$E = \frac{(La)(t)}{MW_{nc}} \left( \frac{\sum_{i=1}^n P_i MW_i}{P_{system} - \sum_{j=1}^m P_j} \right)$ <p> E = mass of HAP emitted  P<sub>system</sub> = absolute pressure of receiving vessel or ejector outlet conditions, if there is no receiver  P<sub>i</sub> = partial pressure of the HAP at the receiver temperature or the ejector outlet conditions  P<sub>j</sub> = partial pressure of condensable (including HAP) at the receiver temperature or the ejector outlet conditions  La = total air leak rate in the system, mass/time  MW<sub>nc</sub> = molecular weight of noncondensable gas  t = time of vacuum operation  MW<sub>i</sub> = molecular weight of the individual HAP in the emission stream, with HAP partial pressures calculated at the temperature of the receiver or ejector outlet, as appropriate </p>
34	$V = \frac{(W_g)(R)(T)}{(P_T)(MW_g)}$ <p> Gas Evolution:  V = volumetric flow rate of gas evolution  W<sub>g</sub> = mass flow rate of gas evolution  R = ideal gas law constant  T = temperature at the exit, absolute  P<sub>T</sub> = vessel pressure  MW<sub>g</sub> = molecular weight of the evolved gas </p>
35	$E = B \times \left( \frac{PS_1}{100 - PS_1} - \frac{PS_2}{100 - PS_2} \right)$ <p> Air Drying:  E = mass of HAP emitted  B = mass of dry solids  PS<sub>1</sub> = HAP in material entering dryer, weight percent  PS<sub>2</sub> = HAP in material exiting dryer, weight percent </p>
36	Empty Vessel Purging:

	$E = \left( \frac{V}{RT} \times \left( \sum_{i=1}^n (P_i)(MW_i) \right) \left( 1 - e^{-Ft/v} \right) \right)$ <p> V = volume of empty vessel  R = ideal gas law constant  T = temperature of the vessel vapor space; absolute  P<sub>i</sub> = partial pressure of the individual HAP at the beginning of the purge  (MW<sub>i</sub>) = molecular weight of the individual HAP  F = flowrate of the purge gas  t = duration of the purge  n = number of HAP compounds in the emission stream  i = identifier for a HAP compound  (Note: The term e<sup>-Ft/v</sup> can be assumed to be 0) </p>
37	$E = \Delta h \times \frac{\sum_{i=1}^n P_i}{P_T - \sum_{j=1}^m P_j} \times MW_{HAP}$ <p> Heating (controlled emissions):  E = mass of HAP emitted  θ? = moles of noncondensable gas displaced  P<sub>T</sub> = pressure in the receiver  P<sub>i</sub> = partial pressure of the individual HAP at the receiver temperature  P<sub>j</sub> = partial pressure of condensable VOC (including HAP) at the receiver temperature  n = number of HAP compounds in the emission stream  MW<sub>HAP</sub> = the average molecular weight of HAP in vapor exiting the receiver, as calculated using Equation 17 of this subpart  m = number of condensable VOC (including HAP) in the emission stream </p>
38	$E = (V_{nc1} - V_{nc2}) \times \frac{\sum_{i=1}^n (P_i)}{P_T - \sum_{j=1}^m (P_j)} \times \frac{P_T}{RT} \times MW_{HAP}$ <p> Depressurization (controlled emissions, 1):  E = mass of HAP vapor emitted  V<sub>nc1</sub> = initial volume of noncondensable in the vessel, corrected to the final pressure, as calculated using Equation 39 of this subpart  V<sub>nc2</sub> = final volume of noncondensable in the vessel, as calculated using Equation 40 of this subpart </p>

	<p> <math>P_i</math> = partial pressure of each individual HAP at the receiver temperature  <math>P_j</math> = partial pressure of each condensable VOC (including HAP) at the receiver temperature  <math>P_T</math> = receiver pressure  <math>T</math> = temperature of the receiver  <math>R</math> = ideal gas law constant  <math>MW_{HAP}</math> = the average molecular weight of HAP calculated using Equation 17 of this subpart with partial pressures determined at the receiver temperature  <math>n</math> = number of HAP compounds in the emission stream  <math>m</math> = number of condensable VOC (including HAP) in the emission stream </p>
39	$V_{nc1} = \frac{VP_{nc1}}{P_T}$ <p>Depressurization (controlled emissions, 2):</p> <p> <math>V_{nc1}</math> = initial volume of noncondensable gas in the vessel  <math>V_{nc2}</math> = final volume of noncondensable gas in the vessel  <math>V</math> = free volume in the vessel being depressurized  <math>P_{nc1}</math> = initial partial pressure of the noncondensable gas, as calculated using Equation 41 of this subpart  <math>P_{nc2}</math> = final partial pressure of the noncondensable gas, as calculated using Equation 42 of this subpart  <math>P_T</math> = pressure of the receiver </p>
40	<p>Depressurization (controlled emissions, 3):</p> $V_{nc2} = \frac{VP_{nc2}}{P_T}$ <p>(same as equation 39)</p>
41	$P_{nc1} = P_1 - \sum_{j=1}^m P_j$ <p>Depressurization (controlled emissions, 4):</p> <p> <math>P_{nc1}</math> = initial partial pressure of the noncondensable gas in the vessel  <math>P_{nc2}</math> = final partial pressure of the noncondensable gas in the vessel  <math>P_1</math> = initial vessel pressure  <math>P_2</math> = final vessel pressure  <math>P_j</math> = partial pressure of each condensable VOC (including HAP) in the vessel  <math>m</math> = number of condensable VOC (including HAP) in the emission stream </p>
42	<p>Depressurization (controlled emissions, 5):</p> $P_{nc2} = P_2 - \sum_{j=1}^m P_j$

	(Same as equation 41)
43	<p>Empty Vessel Purging (controlled emissions):</p> $E = \frac{V}{R} \left( \left( \sum_{i=1}^n \frac{(P_i)_{T_1} (MW_i)}{T_1} \right) (-e^{-Ft/V}) - \left( \sum_{i=1}^n \frac{(P_i)_{T_2} (MW_i)}{T_2} \right) \ln \left( \frac{\sum_{i=1}^n (P_i)_{T_2}}{\sum_{i=1}^n (P_i)_{T_1}} + 1 \right) \right)$ <p> V = volume of empty vessel  R = ideal gas law constant  T<sub>1</sub> = temperature of the vessel vapor space at beginning of purge  T<sub>2</sub> = temperature of the receiver, absolute  (P<sub>i</sub>)<sub>T1</sub> = partial pressure of the individual HAP at the beginning of the purge  (P<sub>i</sub>)<sub>T2</sub> = partial pressure of the individual HAP at the receiver temperature  MW<sub>i</sub> = molecular weight of the individual HAP  F = flowrate of the purge gas  t = duration of the purge  n = number of HAP compounds in the emission stream  i = identifier for a HAP compound </p>



## Appendix PT

### Emissions Performance Testing - Test Methods and Approach

<b>Overview</b>	<p>In complying with emissions control requirements for process vents, tanks, and wastewater emission sources, the O/O has a choice of demonstrating compliance with standards for:</p> <ul style="list-style-type: none"><li>C Organic HAP Mass Removal/Destruction Efficiency,</li><li>C TOC Mass Removal/Destruction Efficiency, or</li><li>C Outlet TOC concentration.</li></ul>
<i>Organic HAP</i>	<p>Organic HAP mass removal/destruction efficiency is determined by comparing the mass rate of organic HAPs leaving the air pollution control device (APCD) to the mass rate entering the APCD. Mass rates are calculated by multiplying organic HAP concentrations by the gas flow rate. Total organic HAP concentration is typically defined as the sum of <u>individual</u> organic HAP compounds (for APCDs controlling solely wastewater emission sources, Organic HAP includes only SHAP and PSHAP compounds).</p>
<i>TOC</i>	<p>TOC concentration is the sum of <u>all</u> organic compounds minus concentrations of methane and ethane. TOC concentrations can be used for calculating efficiency or to demonstrate compliance with the 20 ppmv TOC concentration limit (TOC is almost always referred to in conjunction with demonstrating compliance to 20 ppm TOC standard)</p>
<i>Structure of this Appendix</i>	<p>The list of applicable test methods for demonstrating compliance with the Pharmaceutical MACT standards is listed below. Summaries of each test method are presented. The benefits of selecting a particular method are then discussed.</p>
<b>Demonstrating Compliance with Percent Reduction Standards</b>	<p>For demonstrating compliance with percent reduction standards, the following methods can be used:</p> <ul style="list-style-type: none"><li>C Method 18 - (HAP or TOC) - all control devices</li><li>C Method 25 - (HAP or TOC) - only from combustion sources,</li><li>C Methods 26 or 26A - (HAPs with HCl; TOC with hydrogen halides HCl, HBr and HF or halogens Cl<sub>2</sub> and Br<sub>2</sub>)</li><li>C Method 25A - (HAP or TOC) - only under any of the following limited conditions:<ul style="list-style-type: none"><li>1. There is only one compound known to exist,</li><li>2. Where the organic compounds consist of only hydrogen and carbon,</li></ul></li></ul>

3. Where relative percentages of the compounds are known or can be determined and FID responses to the compounds are known,
4. Where a consistent mixture of the compounds exist both before and after the control device and only the relative concentrations are to be assessed, or
5. Where the FID can be calibrated against mass standards of the compounds emitted (i.e., predominant HAP compound)

**Demonstrating Compliance with TOC Standards**

For demonstrating compliance with TOC standard, the following methods can be used:

- C Method 18- conforming to performance specification 9 (40 CFR 60 App B),
- C Method 25A - calibrated with either methane or the predominant HAP and meeting performance specification 8, or
- C Method 26 - for measuring hydrogen halide concentrations (if present)

***Q and A***

***Q Do I have to use one of the listed methods for determining concentrations of HAP or TOC?***

***A. No. Any method which has been validated by EPA validation Method 301 (§40 CFR 63 Appendix A) can also be used. This is especially the case for certain HAPs that cannot be measured by Method 18 or 25A. Formaldehyde, for example, does not respond well to a FID used in Method 25A and sometimes in Method 18. Phenol is another example of a compound very difficult to sample and analyze using Method 18 procedures.***

**Method 18**

Method 18 (Measurement of Gaseous Organic Compound Emissions by Gas Chromatography [discrete GC analyses for individual HAPs conducted either on-site or off-site]) is suitable for measuring concentrations of many organic HAPs. The method uses Gas Chromatography (GC) coupled with any suitable detector. By using the GC separation capability, Method 18 can quantify concentrations of individual compounds. Sample procedures are listed as follows:

- C Integrated Bag Sampling. Configurations include evacuated container, direct pump sample, or other (heated, or diluted bag configurations, etc.)

- C Direct Interface (heated tubing from stack to instrument)
- C Dilution Interface, or
- C Sorbent Tube

There is no criterion for how quickly the sample must be analyzed, so for bag (container) sampling, it is possible to analyze samples off-site (However, extensive QA procedures must be performed showing that analytical recoveries are not biased by this lapse in time). Typically, analyses are conducted on-site, during sampling.

The method is only semi-continuous at best, because even with direct interface sampling which calls for extracting a continuous sample stream from the stack, each analyses takes several minutes to conduct.

**NOTE:** TOC, organic HAP, hydrogen halide and halogen concentrations from combustion control devices must be corrected to 3% O<sub>2</sub>, if supplemental gases are added to the vent stream or manifold:

$$C_c = C_m \left( \frac{17.9}{20.9\% O_2} \right)$$

Where

- C<sub>c</sub> = concentration of TOC, total organic HAP, or hydrogen halide and halogen corrected to 3 percent oxygen, dry basis, ppmv
- C<sub>m</sub> = total concentration of TOC or total organic HAP or hydrogen halide and halogen in vented gas stream, average of samples, dry basis, ppmv
- %O<sub>2d</sub> = concentration of oxygen measured in vented gas stream, dry basis, percent by volume

Supplemental gases are defined in §63.1251 and include gases that are not defined as process vents, or closed-vent systems from wastewater units, storage tanks, or equipment components; they contain less than 50 ppmv TOC. Air required to operate combustion device burners is not considered a supplemental gas. Concentration values to be used as an intermediates for calculating mass rates for efficiency determinations do not need to be corrected 3% O<sub>2</sub>.

**NOTE:** TOC, organic HAP, or hydrogen halide and halogen concentrations from non-combustion devices must be corrected if supplemental gases are added:

$$C_a = C_m \left( \frac{V_s \% V_a}{V_a} \right)$$

Where:

$C_a$  = corrected outlet TOC, organic HAP, and hydrogen halides and halogens concentration, dry basis, ppmv

$C_m$  = actual TOC, organic HAP, and hydrogen halide and halogens concentration measured at control device outlet, dry basis, ppmv

$V_a$  = total volumetric flow rate of all gas streams vented to the control device, except supplemental gases

$V_s$  = total volumetric flow rate of supplemental gases

### Method 18 Calibration and QA Criteria

**Calibration:** A minimum of 3 gas standards/compound must be used to prepare calibration curves. Duplicate analyses of each standard must agree to within 5% of their mean. Standards must be analyzed both before and after sample analyses. Use an average of the 2 curves to determine sample concentration. If the 2 curves differ by more than 5% from their mean, report final results using both curves (resulting in 2 sample data sets)

**Sample Analyses:-** Final bag analyses concentration equals the average of 2 replicate analyses. Replicate peak areas must agree within 5% of their average (maybe difficult for direct interface if process is changing and at least several minutes lapse between analyses)

**Dilution System Check:** For dilution systems, a single calibration gas (high) must be directed through entire dilution system. Resulting values should be within 10% of expected.

**Performance Audits:** Audit analyses of 2 gases (high and low) must be within 10% of true value. If results are not within 10%, the audit supervisor determines corrective action (correct instrumental problems and re-run audit, numerically correct biased data set, etc).

**Recovery Study:** For direct interface and dilution systems, direct mid level calibration gases through entire system. Replicate analyses should agree to within 5% of their mean and within 10% of the reading determined when gas are challenged directly to analyzer (sample bias). For bag sampling, spike a sample bag, to 40-60% of average sample concentration or 5 times the MDL (if sample not detected). From these results, the calculated a R value should be within 0.7 - 1.3. R is calculated as shown in Section 7.6.2 of Method 18. For sorbent tubes, 2 sample probes (tubes) are located adjacently in the stack and a sample taken. One is spiked with liquid or gaseous compounds while the other is not. From these results, the calculated R value should be within 0.7 - 1.3.

### Additional Method 18 calibration and QA criteria when used for the 20 ppm TOC Standard (per Performance Specification 9, 40 CFR 60 Appendix B)

**Calibration Gases:** Low level 40-60% of measured concentration (or 4-5x MDL),  
Mid level 90-110% of measured concentration  
High level 140-160% of measured concentration

**Calibration Error:** Calibration error checks must be performed for each target compound every 24 hours for each of the 3 standards. Observed concentration must be within 10% of actual value.

**Calibration Precision and Linearity:** Standards must be analyzed in triplicate. All must be within 5% of mean and an  $R^2$  of  $> 0.995$

**Measurement Frequency:** Sample time constant, T, must be less than 5 minutes or the sample frequency specified in the applicable regulation. T is calculated using equation 3 in PS 9.

**Performance Audits:** Same as above

### ***Q and A***

***Q Does an O/O really have to conduct all the pre-test method development listed in Method 18 ?***

***A The objectives of the Method 18 preliminary method development are to 1) determine all target compounds. 2) optimize GC operating parameters and 3) develop acceptable QA procedures. Much of the method development information and QA procedures can be determined from past testing experience and existing laboratory methods. Potential target compounds can be revealed by interviewing plant personnel who have knowledge of the process being tested. However, during testing, compounds with GC peaks that have peak areas greater than 5% of the total peak area must be identified. Therefore, it is extremely important to develop the test method, prior to conducting the test, that will adequately quantify all possible target compounds. However, as long as the final Method 18 calibration and QA criteria are met during the test program, most administrators will not require such an extensive pre-test work up as is written up in the method.***

### ***Method 25A***

Method 25A does not have the capability of separating and quantifying individual compounds. It measures total organic gas concentration on a continuous basis using a flame ionization detector (FID). The FID is calibrated using a single calibration compound. The Pharmaceutical MACT allows the O/O to use either methane or the most predominant HAP as a calibration gas. Methane is used routinely for Method 25A calibrations (TOC/Methane). However, TOC/Methane results can be relatively high when compared with other calibration techniques due to differences in various compound FID relative response factors (RRF) as discussed below:

- C TOC/Methane concentrations respond to a hydrocarbon compound at 1 ppm per 1 ppm of compound multiplied the number of carbon atoms in the compound. For example 4 ppm of benzene ( $C_6H_6$ ) would respond as 24 ppm methane (4 x 6 carbon atoms/molecule). If the HAPs do not consist strictly of hydrogen and carbon (i.e., contain alcohols, aldehydes, nitrogen, halogens, or other) the TOC/Methane RRF will be somewhat less than the 1 per number of carbon atoms/molecule. For example, if 20 ppm ethanol ( $C_2H_5OH$ ) were present, a methane calibrated analyzer would respond at ~30 ppm TOC/methane (RRF = 1.5 ppm methane/ppm ethanol).
- C Method 25A can be calibrated using the predominant HAP. For

the above benzene scenario, if TOC was determined by Method 25A calibrated with benzene, the resulting TOC/Benzene value would be 4 ppm (vs 24 ppm as TOC/Methane) ,

In determining which calibration gas to use, it should be remembered that calibration gases are not available for all HAP compounds, and the prices of non-methane calibration gases can be high.

#### ***Q and A***

***Q***      ***What are the requirements for using the predominant HAP as the Method 25A calibration gas ?***

***A***      *The following criteria must be met in order to use the predominant HAP as the Method 25A calibration gas:*

***C***      *The HAP is the single organic HAP representing the large percent by volume*

***C***      *The response from the high calibration gas is at least 20 times the standard deviation of the response from the zero calibration gas when the instrument is zeroed on the most sensitive scale*

***C***      *The span value of the analyzer must be less than 100 ppmv*

#### ***Measuring Methane & Ethane Concentrations***

For TOC determinations, concentrations of methane and ethane should be subtracted from the total organic concentration. Some of the newer Method 25A analyzers can incorporate this into their operation, however, if methane values are substantial it may be better to analyze for methane and ethane separately using Method 18 or other technique (there is no required method listed in the rule for determining methane concentrations for calculating nonmethane organic concentrations, however, the planned procedure should be approved by the test plan administrator). Methane concentrations can also be approximated by techniques such as filtering the Method 25A sample stream through a charcoal tube (to remove all compounds but methane). Some sources, especially combustion sources fired on natural gas, may contain a considerable amount of methane (>50% of TOC). Quantities of ethane are usually not as high. If test costs include a methane determination by Method 18, it may be a good idea to include speciated organics in the analysis as well. In this way, if the

TOC/Methane values do not demonstrate compliance, the O/O may be able recalculate TOC using Method 18 data.

WARNING: If any changes are made to any performance testing procedures during the test program, the data may not be accepted by the regulatory agency. However, if the test engineer explains the logic behind the changes to the observer and has him/her “sign off” on the changes (in a log book, etc), the test results may be accepted.

**Easy Calculation:** TOC concentrations are calculated as the sum concentrations of all organics in the gas stream minus those of methane and ethane. However, if TOC is determined by Method 25 or 25A, the resulting measurement values already reflect total organic concentration, so that no sums have to be taken. Only methane and ethane concentrations need to be subtracted from these values.



**Method 25A Calibration and QA criteria:**

Calibration: A minimum of 4 gas standards concentrations as follows:

- C zero gas = < 0.1 ppmv organics or < 0.1% span, (whichever is greater)
- C low level = 25-35% of span
- C mid level = 45-55% of span
- C high level = 80-90% of span

**Zero Drift:** Introduce zero level gases after every test, or hourly during test. Must be less than  $\pm 3\%$  of span (gas directed through entire sample system)

**Calibration Drift:** Introduce mid level gases after every test, or hourly during test. Must be less than  $\pm 3\%$  of span (gas directed through entire sample system)

**Calibration Error:** Introduce low and mid level gases before start of test. Must be less than  $\pm 5\%$  of calibration gas value (gas directed through entire sample system)

**Corrective Action:** If CE is unacceptable, do not start testing until problem is corrected and CE is acceptable. If CD is unacceptable, either invalidate test results or recalibrate instrument and report results using both sets of calibration data.

**Response Time:** Measured 1/test program

**Additional Calibration and QA criteria when used for the 20 ppm TOC standard (per Performance Specification 8, 40 CFR 60 Appendix B).**

**Data Recorder Scale:** For uncontrolled sources = 1.25 to 2 times the average potential level, For controlled sources = 1.5 times the pollutant concentration corresponding to the emissions standard

**Calibration Drift:**  $\pm 2.5\%$  of span (gas directed through entire sample system)

**Relative Accuracy:** < 20 % mean value of the reference method test data in units of the applicable emissions standard, or 10% of the applicable standard, whichever is greater.

*Method 25*

Method 25 measures Total Gaseous Nonmethane Organic Emissions as Carbon. A sample of gas is extracted from the stack, pulled through a cryogenic trap to collect the higher molecular weight organic compounds, and then into an evacuated canister, to collect the lower molecular weight organic compounds. In principle, the analysis is then completed on both fractions in the following steps:

1. Measure sample methane and CO<sub>2</sub> and concentration (background)
2. Oxidize all organics to CO<sub>2</sub> and H<sub>2</sub>O,
3. Catalytically reduce CO<sub>2</sub> to CH<sub>4</sub>, and
4. Measure residual CH<sub>4</sub> concentration.

The difference between the background CH<sub>4</sub> concentration from the oxidized/reduced CH<sub>4</sub> fraction is attributable to the concentrations of organic compounds in the gas stream. This method does not have a response factor bias as does Method 25A, but has a detection limit of 50 ppmC (parts per million carbon, same as ppm as methane). For many process/control device situations, this detection limit is too high to allow control efficiency compliance to be demonstrated.

#### *Method 26*

Method 26, Determination of Hydrogen Chloride from Stationary Sources, uses aqueous absorbing solutions to collect and quantify hydrogen chloride (HCl). It cannot be used for measuring concentrations of organics. It can be used for determining removal efficiencies of HCl in control efficiency demonstrations or halogenated compounds for the 20 ppm TOC/halogen halide concentration requirements.

#### ***Q and A***

***Q Which parameters (Organic HAP or TOC) should an O/O use to demonstrate compliance ?***

***A The selection of whether to use Organic HAP removal efficiency standard or TOC concentration standard to demonstrate APCD compliance is case specific. For some cases where the APCD is functioning well and is controlling TOC to levels much lower than 20 ppm TOC/Methane, then TOC as measured by Method 25A is the simplest and least costly choice. For cases where the margin of compliance is closer, it may be a “safer bet” to measure Total Organic HAP at the inlet and outlet for removal efficiency determinations.***

#### ***Compounds not Included in Wastewater APCD Tests***

For wastewater sources, the total Organic HAPs method target compounds need not include compounds not used or produced, compounds in wastewater POD that are < 1 ppmw, or compounds which are not detected in wastewater when detection limits are not greater than < 1 ppmw.

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## How is gas flow rate measured ?

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### **Flow Rate Determinations**

Vent gas flow rate must be measured for determining Organic HAP mass rates. Section 1257(b) states that EPA Method 2, 2A, 2C or 2D must be used for measuring volumetric flow rates. However, some of these methods may not be appropriate for low flow or batch processes as discussed below.

#### *Method 2*

Method 2 incorporates the use of an S type pitot tube to measure velocity pressure drop and gas velocity. The gas velocity is then multiplied by the duct cross sectional area to determine flow rate. Incorporated into Method 2 are measurements of O<sub>2</sub>/CO<sub>2</sub> concentrations, gas temperature, and gas moisture content. Method 2 works well for measuring fairly stable flows with a measurable pressure drop (not too low). If velocity pressures are lower than 0.05 inches water column (in. wc), a more sensitive pressure gauge than what is described in Method 2 must be used (or use a different flow measurement technique). Method 2 is conducted manually with discrete measurements taken periodically. If flow rate fluctuates, periodic measurements may not capture all flow rate episodes which could result in a biased flow rate average.

#### *Method 2A - 2E*

Method 2A -2E are alternative flow measurement methods for situations where Method 2 is not recommended. They are entitled as follows:

- C 2A = Direct measurement of gas volume through pipe and small ducts (volume meters),
- C 2B = Determination of exhaust gas volume flow from gasoline vapor incinerators
- C 2C = Determination of gas velocity and volumetric flow rate in small stacks or ducts (standard pitot)
- C 2D = Measurement of gas volumetric flow rates in small pipes or ducts (orifice plates, rotameters, other),
- C 2E = Determination of gas: gas production flow rate

#### *Alternative Flow Monitoring Techniques*

The above alternative Method 2 procedures are suitable for many situations. Most of them incorporate visual observation of pressure other measurement. For batch processes having very variable flow rate, it may be necessary to use the above methods with an automated measuring device capable of sending the measurement signal to a continuous data acquisition system (i.e., pressure transducer, temperature thermocouple, anemometer, etc). Continuous readings of flow rate could then be acquired and accurate averages calculated. If the test firm is using a

continuous emissions monitoring systems (CEMS) for Method 25A tests, it is not much more difficult to incorporate continuous flow monitoring into their data acquisition system. Alternative flow rate measurement techniques may be approved as well. For batch processes, tracer gas injection (SO<sub>2</sub>, CO, etc) with dilution monitoring works well and provides continuous flow rate data (per Alternative EPA Method Alt-012).

*Cyclonic Flow  
Measurements*

For instances of cyclonic flow, EPA Method 1 recommends that EPA Method 2 not be used for determining flow rate. In these cases, there are alternative methods which can be used, if approved by the administrator (i.e, Draft Method 2F- Alternative Method ATM-015).

*O<sub>2</sub>/CO<sub>2</sub>  
Measurements*

Oxygen and carbon dioxide concentrations must be measured to incorporate into gas flow rate calculations (if velocity pressure flow measurement technique is used). Also, if the TOC compliance option is being used on a combustion APCD, TOC values must be corrected to 3% O<sub>2</sub>. Section 63.1257(b)(3) states that EPA Method 3 must be used for gas analysis. EPA Method 3 determines O<sub>2</sub> and CO<sub>2</sub> using either a Fyrite™ or an Orsat™ analyzer. If the O<sub>2</sub> measurement is needed for TOC correction to 3% O<sub>2</sub>, then a Fyrite™ can not be used. Using an Orsat™ analyzer for O<sub>2</sub> measurements can be time consuming and has potential for error due to leaks and operator error. It is more simple and technically sound to conduct O<sub>2</sub> measurements using CEMS by EPA Method 3A.

*Moisture  
Determination*

Gas moisture content is incorporated into flow rate calculations (if velocity pressure flow measurement techniques are used) and Method 18 & 25A analyses ( to correct TOC values from a wet basis to a dry basis). EPA Method 4 should be used to determine moisture. This procedure calls for extracting a gas stream from the duct and bubbling it through chilled water and pre-weighed silica gel desiccant. Moisture is determined by comparing the volume of moisture collected by the water and silica gel to the volume of gas sampled. If the stream is saturated, moisture content is determined by measuring gas temperature and using a psychometric chart or saturation vapor pressure tables. Approximation techniques such as wet-bulb/dry bulb procedures can only be used if it is shown to be within 1% of Method 4 techniques.

*EPA Web Site*

Further details can be found in the EPA reference methods which can be downloaded from the EPA TTN bulletin board at <http://www.epa.gov/ttn/emc/promgate.html>.

**General Approach  
to Performance  
Testing**

If the facility is required to conduct performance testing, it is important to understand the distinct areas of responsibility. Some tasks should be handled by the vendor, however, the ultimate responsibility is with the plant engineer. The discussion provides a set of steps that can be followed in planning and conducting a performance test.

## **Steps in Planning and Conducting a Performance Test Program**

### **Planning, Operating Conditions:**

1. Select how the process(es) will be operated during the test program (i.e., absolute worst-case, or hypothetical worst-case)
  - If the above entails precise timing of multiple process events, verify that the approach is feasible,
2. Select how the APCD or wastewater treatment equipment will be operated during the test program,
3. Select which process, APCD, and wastewater treatment parameters to monitor,
4. Determine how the above parameters will be monitored and which ones are candidate parameters for monitoring on an on-going basis.

### **Planning, Test Objectives:**

5. Determine pollutant concentration test methods and detection limits,
6. Verify detection limits are sufficient for demonstrating compliance,
7. Select flow monitoring methods and devices,
8. Verify that expected costs for above scope are within a reasonable testing budget.

### **Executing the Pre-Test Survey:**

12. Meet on-site with the vendor to confirm approach on all of the above,
13. Discuss and confirm all Health & Safety precautions and required procedures,
14. Confirm vendors needs for mobile lab parking, access to sample sites, utilities, process coordination (start and stop times),
15. Confirm what type of process data will be collected and who will collect it, and,
16. Walkthrough facility examining sample sites and process data collection points.

### **Executing the Test Program:**

17. Confirm expected testing schedule and logistics with vendor on equipment set-up day,
18. Conduct test program,
19. Verify collection of all process data, and
20. Collect copies of field data sheets & sample log or chain of custody.

### **Data Reduction and Reporting:**

21. Verify receipt of samples by laboratory
22. Confirm expected sample analysis date and preliminary report date,
23. Reduce all on-site data (flows, sample volumes, process data),
24. Incorporate analytical data and prepare preliminary report,
25. Review preliminary report,
26. Incorporate comments and finalize report.

## Selecting the Testing Firm

There are many testing firms highly qualified to conduct sampling and analyses for gas phase and water phase pollutants. In selecting a vendor the following items should be considered:

1. Determine if the testing firm should provide engineering services in addition to testing. If so, should they include both process engineering as well as control device/treatment equipment engineering ?
2. Prepare scope of work for the RFP and be explicit in:
  - what are the target compounds,
  - what test methods are not suitable
  - What detection limits are needed (provide expected concentrations and flow rates),
  - What is the available testing window is (hours of the day),
  - Whether the vendor should provide a process interface person for process data collection (do not expect the vendor to provide this without him costing it in)
  - What type of data reduction/reporting is desired (i.e., deliver two types of reports - sanitized and unsanitized, what types of averages should be calculated for complex scenarios, how to combine process data and emissions data, graphics, etc.)
3. Have vendors submit cost proposals including costs for baseline scope of work and on-site field team costs (\$/hr) for possible add-on tasks.
4. Review proposals and select testing firm.

Note on Detection limits - Make sure the vendor states what the detection limits will be (concentration and mass rate for a given flow rate) and see if these values will suit your needs. For example, if your inlet loading to an APCD is estimated to be 20 lbs/hr HAPs, and your detection limit at the outlet is < 5 lbs/hr, the highest removal efficiency that can be demonstrated is 75%. If this is the case, a different test method with a lower detection may be needed at the APCD outlet.

Note on Process Data Collection: There always seems to be confusion surrounding the role of process/testing interface person. The plant people know the facility best however, the test people know how the testing will be conducted (timing). It is important to establish what roles will be played by whom.

## Appendix WWT

### Wastewater Treatment Performance Testing - Test Methods and Approach Overview

Wastewater Treatment (WWT) performance testing must be used to demonstrate compliance for open biological treatment systems. Either WWT testing or WWT design evaluation can be used for closed biological or nonbiological treatment systems. There are six wastewater performance test procedures stipulated in §63.1257(e)(2)(iii) B-G listed as follows:

- C wastewater concentration limits (**noncombustion** treatment)[§63.1257(e)(2)(iii)(B)]
- C wastewater mass removal/destruction efficiency limits:
  - **noncombustion & non biological** treatment [§63.1257(e)(2)(iii)(C)]
  - **combustion** treatment [§63.1257(e)(2)(iii)(D)]
  - **biological (open or closed)** [§63.1257(e)(2)(iii)(E & F)]
  - **closed biological** only [§63.1257(e)(2)(iii)(G)]

The six performance testing procedures are similar in that they require:

- C three 1-hour test runs,
- C grab wastewater sampling or integrated wastewater sampling at approximately equally spaced time intervals during each hour of the three 1-hour tests,
- C wastewater sampling per §63.1257(b)(10)(vi), that calls for sampling procedures that minimize emissions, such as 40 CFR 60 Appendix A Method 25D sampling guidelines (collecting the sample through a cooling coil into a jar containing Polyethylene Glycol, PEG)
- C wastewater flow measurements concurrent with concentration sampling,
- C Separate inlet and outlet flow measurements, if the outlet flow is higher. If the outlet flow is not greater than the inlet, then a single flow measurement is satisfactory, at either the inlet or outlet.

$F_{bio}$

For **biological** treatment demonstrations, the mass removal/destruction efficiency determinations incorporate the use of a site specific degradation factor  $F_{bio}$  (closed biological can use either methods in §63.1257(e)(2)(iii)(E) & (F), which incorporate  $F_{bio}$ , or G which does not).  $F_{bio}$  is an indication of what fraction of total organics in solution biodegrade, as opposed to being emitted or remaining in the effluent. The first step in determining  $F_{bio}$  is to measure the compound-specific degradation rate  $f_{bio}$  using procedures found in Appendix C to Part 63. These are:

- 1A. M304A - Determine site specific, biodegradation factor using bench scale laboratory set up/ air vent (use instead of 304B when



compounds react or hydrolyze in the scrubber of Method 304B).

- 1B. M304B - Same as previous w/ scrubber and is not vented (when Henry's Law constants are not known.)
2. Site specific performance data with and without biodegradation used to calculate  $F_{bio}$ .
3. Any of the above 3 methods or using inlet and outlet concentration measurements coupled with calculation such as a computer model (i.e, Water7, TOXCHEM, BASTE, etc).
4. Batch treatability tests

NOTE: For non-enhanced bio treatment, use  $f_{bio}$  method 1, 2, or 4 above. For enhanced bio treatment, use  $f_{bio}$  method 1, 2, 3, or 4 for PSHAPs. For SHAPs use  $K_1$  = Table 9 values & follow Appendix C, Form III or use  $f_{bio}$  methods 1, 2, 3, or 4.

The total stream  $F_{bio}$  is then determined by multiplying each compound specific  $f_{bio}$  by the compound mass flow rate in the wastewater stream, summing all compound specific  $f_{bio} \times$  mass flow products and then dividing by the total organic mass flow in the wastewater stream. Further details can be found in the Appendix C reference methods which can be downloaded from the EPA TTN bulletin board at <http://www.epa.gov/ttn/emc/promgate.html>.

For further guidance on "thoroughly mixed" biological treatment units, see guidance at <http://www.epa.gov/ttn/oarpg/t3/reports/guidfn.pdf>.

**Note on choosing biological treatment compliance demonstration procedure:**

**Closed Biological** - If the O/O chooses closed biological treatment and demonstrates compliance using §63.1257(2)(iii)(E) or (F), then the treatment process is not subject to wastewater storage tank or surface impoundment vapor suppression standards.

**Open Biological** - If the O/O chooses open biological treatment, the treatment process need not be covered and vented to a control device. Also, if compliance is demonstrated by §63.1257(2)(iii)(E) or (F), the treatment process is also not subject to wastewater storage tank or surface impoundment vapor suppression standards.

### *Mass Removal/Destruction Efficiency for Biological Systems*

Procedures are given for determining mass removal/destruction efficiency from the following 2 biological treatment configurations:

1. mass destruction/removal efficiency is determined across a biological treatment system only, or
2. mass destruction/removal efficiency is determined across a series of treatment processes

Compliance is demonstrated if destruction/removal efficiency, E, is 95% or greater. For case 1 above, mass removal/destruction efficiency (E) is equal to  $F_{\text{bio}}$ . In the second case, use the equation below. (Equation 50 from the rule.)

$$E = \frac{\text{Nonbiotreatment HAP load removal \% Biotreatment HAP load removal}}{\text{Total influent HAP load}}$$

$$= \frac{\sum_{i=1}^n \left( \text{QMW}_{a,i} - \text{QMW}_{b,i} \right) \% \text{QMW}_{\text{bio}} (F_{\text{bio}})}{\text{QMW}_{\text{all}}}$$

$\text{QMW}_{a,i}$  = the soluble and/or partially soluble HAP load entering a treatment process segment

$\text{QMW}_{b,i}$  = the soluble and/or partially soluble HAP load exiting a treatment process segment

$n$  = the number of treatment process segments

$i$  = identifier for a treatment process element

$\text{QMW}_{\text{bio}}$  = the inlet load of soluble and/or partially soluble HAP to the biological treatment process. The inlet is defined in accordance with 63.1257 (e)(2)(iii)(A)(6). If complying with 63.1257 (e)(2)(iii)(A)(6)(ii) (i.e., the inlet to the equalization tank is considered to be the inlet to the biological treatment process) of this section,  $\text{QMW}_{\text{bio}}$  is equal to  $\text{QMW}_{b,n}$

$F_{\text{bio}}$  = site-specific fraction of soluble and/or partially soluble HAP compounds biodegraded.

$\text{QMW}_{\text{all}}$  = the total soluble and/or partially soluble HAP load to be treated.

If wastewater is conveyed by hard piping, mass removal/destruction efficiency is

determined across the combination of all treatment processes. Owners/operators may conduct the performance test across each series of treatment processes (§63.1257(e)(2)(iii)(A)(5)(i) ) OR conduct the test over each individual treatment process in the series of processes and sum them together (§63.1257(e)(2)(iii)(A)(5)(ii) ). If wastewater is not conveyed by hard piping, efficiency must be determined across each treatment process with total efficiency equal to the sum of efficiencies from each component process. In this manner, the owner or operator does not get credit for fugitive emissions that may occur between treatment process segments.

- Equalization Tank*    The inlet to the biological process may be considered the inlet to the equalization tank if:
- Wastewater is conveyed by hard piping from last treatment process or POD to equalization tank, or
  - Wastewater is conveyed by hard piping from equalization tank to biological treatment process, or
  - Equalization tank is equipped with a fixed roof/closed vent system/APCD.

- Test Plan*            A site specific test plan must be prepared addressing the following:
- C        Test program summary,
  - C        Test schedule,
  - C        Data quality objectives (pretest expectations of precision, accuracy and completeness of data),
  - C        Internal and External QA programs (internal QA includes assessment of data precision, external includes activities such as performance audits), and
  - C        An emission profile must also be included if tests are being conducted on a control device which controls process vents from a batch process.

The test plan must be submitted to the administrator at least 60 days before the scheduled test date.

- Sample Plan*        All compliance procedures listed above require a sample plan to be developed and kept on-site. The sample handling procedures must be aimed at minimizing the loss of volatiles from the sample solution. In summary, the following tasks must be considered:
- C        Use Procedures in Chapter 9 of SW-846 for developing sampling plan,
  - C        Sample location should be representative of unexposed waste (where waste has minimum opportunity to volatilize to atmosphere)

- C Collect the sample through a tap or use a submerged container (if a tap is impractical)
- C Distinguish sampling procedures for single phase or well mixed waste versus multi-phase waste
- C Collected through a chilled coil into a chilled polyethylene glycol (PEG) solution or chilled VOA tubes
- C Determine target compound recovery efficiency during sample analyses

Three, 1-hour long sample runs must be performed at representative process unit operation and representative treatment process. The owner/operator may collect grab samples or composite samples. If the treatment process operates at multiple representative conditions, testing at each condition is not necessary. Calculations or engineering evaluations can be used to supplement test results to demonstrate compliance over the entire range of operation.

*Analytical Summary* Analyses should be completed using Method 305, 624, 625, 8270, 1624, 1625, 1666, 1671 or other validated method. For demonstrating compliance with wastewater concentration limits, either Method 305 should be used or another method with the results multiplied by the compound specific fraction Measured ( $F_m$ ) values. For the purposes of this discussion, these types of wastewater concentrations will be known as wastewater Emission Potential Concentrations (EPC). Analytical techniques for concentrations to be used in calculating mass rates are not EPC values. If Method 305 is used for a mass rate concentration type, the result must be divided by the appropriate  $F_m$  value. Results from other analytical techniques are not adjusted.  $F_m$  values are listed in the following Table. (See page 8-27 for a table on use of  $F_m$  values).

TABLE WWT-2 TO SUBPART GGG. FRACTION MEASURED ( $F_m$ )  
FOR HAP COMPOUNDS IN WASTEWATER STREAMS

Chemical name	CAS No. <sup>a</sup>	$F_m$
Acetaldehyde	75070	1.00
Acetonitrile	75058	0.99
Acetophenone	98862	0.31
Acrolein	107028	1.00
Acrylonitrile	107131	1.00
Allyl chloride	107051	1.00
Benzene	71432	1.00
Benzyl chloride	100447	1.00

TABLE WWT-2 TO SUBPART GGG. FRACTION MEASURED ( $F_m$ )  
FOR HAP COMPOUNDS IN WASTEWATER STREAMS

Chemical name	CAS No. <sup>a</sup>	$F_m$
Biphenyl	92524	0.86
Bromoform	75252	1.00
Butadiene (1,3-)	106990	1.00
Carbon disulfide	75150	1.00
Carbon tetrachloride	56235	1.00
Chlorobenzene	108907	0.96
Chloroform	67663	1.00
Chloroprene (2-Chloro-1,3-butadiene)	126998	1.00
Cumene	98828	1.00
Dichlorobenzene (p-1,4-)	106467	1.00
Dichloroethane (1,2-) (Ethylene dichloride)	107062	1.00
Dichloroethyl ether (Bis(2-Chloroethyl ether))	111444	0.76
Dichloropropene (1,3-)	542756	1.00
Diethyl sulfate	64675	0.0025
Dimethyl sulfate	77781	0.086
Dimethylaniline (N,N-)	121697	0.00080
Dimethylhydrazine (1,1-)	57147	0.38
Dinitrophenol (2,4-)	51285	0.0077
Dinitrotoluene (2,4-)	121142	0.085
Dioxane (1,4-) (1,4-Diethyleneoxide)	123911	0.87
Epichlorohydrin(1-Chloro-2,3-epoxypropane)	106898	0.94
Ethyl acrylate	140885	1.00
Ethylbenzene	100414	1.00
Ethyl chloride (Chloroethane)	75003	1.00
Ethylene dibromide (Dibromomethane)	106934	1.00
Ethylene glycol dimethyl ether	110714	0.86
Ethylene glycol monobutyl ether acetate	112072	0.043
Ethylene glycol monomethyl ether acetate	110496	0.093
Ethylene oxide	75218	1.00

TABLE WWT-2 TO SUBPART GGG. FRACTION MEASURED ( $F_m$ )  
FOR HAP COMPOUNDS IN WASTEWATER STREAMS

Chemical name	CAS No. <sup>a</sup>	$F_m$
Ethylidene dichloride (1,1-Dichloroethane)	75343	1.00
Hexachlorobenzene	118741	0.97
Hexachlorobutadiene	87683	0.88
Hexachloroethane	67721	0.50
Hexane	110543	1.00
Isophorone	78591	0.47
Methanol	67561	0.85
Methyl bromide (Bromomethane)	74839	1.00
Methyl chloride (Chloromethane)	74873	1.00
Methyl ethyl ketone (2-Butanone)	78933	0.99
Methyl isobutyl ketone (Hexone)	108101	0.98
Methyl methacrylate	80626	1.00
Methyl tert-butyl ether	1634044	1.00
Methylene chloride (Dichloromethane)	75092	1.00
Naphthalene	91203	0.99
Nitrobenzene	98953	0.39
Nitropropane (2-)	79469	0.99
Phosgene	75445	1.00
Propionaldehyde	123386	1.00
Propylene dichloride (1,2-Dichloropropane)	78875	1.00
Propylene oxide	75569	1.00
Styrene	100425	1.00
Tetrachloroethane (1,1,2,2-)	79345	1.00
Tetrachloroethylene (Perchloroethylene)	127184	1.00
Toluene	108883	1.00
Toluidine (o-)	95534	0.15
Trichlorobenzene (1,2,4-)	120821	1.00
Trichloroethane (1,1,1-) (Methyl chloroform)	71556	1.00

TABLE WWT-2 TO SUBPART GGG. FRACTION MEASURED ( $F_m$ )  
FOR HAP COMPOUNDS IN WASTEWATER STREAMS

Chemical name	CAS No. <sup>a</sup>	$F_m$
Trichloroethane (1,1,2-) (Vinyl Trichloride)	79005	0.98
Trichloroethylene	79016	1.00
Trichlorophenol (2,4,5-)	95954	1.00
Triethylamine	121448	1.00
Trimethylpentane (2,2,4-)	540841	1.00
Vinyl acetate	108054	1.00
Vinyl chloride (Chloroethylene)	75014	1.00
Vinylidene chloride (1,1-Dichloroethylene)	75354	1.00
Xylene (m-)	108383	1.00
Xylene (o-)	95476	1.00
Xylene (p-)	106423	1.00

<sup>a</sup>CAS numbers refer to the Chemical Abstracts Service registry number assigned to specific compounds, isomers, or mixtures of compounds.

**Flow Measurement** Wastewater (and vent gas) flow measurements are needed to calculate HAP mass rates. Flow measurements should be made during the same period that concentration samples are being collected. If samples are being collected over an hour-long period, enough flow measurements should be taken during that hour so that an accurate flow rate average can be calculated. If flow is constant, the flow may only need to be measured once per test run. However, if flow rate is variable, multiple flow measurements may need to be taken. Separate wastewater inlet and outlet flow measurements must be made unless a) the inlet flow is higher, then a single flow measurement device is satisfactory at either the inlet or outlet or b) the treatment process is an open or closed biological process then only the inlet flow must be measured for the performance test (§63.1257(e)(2)(iii)(E)(2) and (G)). Gas flow rate must be measured by methods stipulated in the rule as discussed in **Appendix PT**. No wastewater flow measurement methods are stipulated in the rule.

**Q. How should treatment device residence time be considered ?**

- A.** Unlike an emissions control device, which has a residence time of a few seconds, the residence time of a wastewater stream flowing through a treatment plant may be much longer. In order to determine treatment efficiency, the treatment plant inlet and outlet PSHAP and SHAP mass rates must be measured on the same “slug” of wastewater flowing through the treatment plant. For example, if the residence time is 30 minutes, the outlet sample should not be collected until after 30 minutes have elapsed since collection of the inlet sample. An even more complicated scenario is when wastewater flow is not constant. Calculations should be made to determine the volume of wastewater which flows by the inlet sample point during inlet sampling, determine the exact treatment plant residence time, and commence outlet sampling after that residence time has elapsed.

*Exempt Compounds* For wastewater sources, the total Organic HAPs method target compounds need not include compounds not used or produced, compounds in wastewater that are < 1 ppmw, or compounds that are not detected in wastewater when detection limits are not greater than < 1 ppmw. Also, as for control devices controlling only wastewater emissions, the target compounds are only PSHAPs and SHAPs and do not include other HAPs.